FULL PAPER
PPS
www.rsc.org/pps

A diffuse reflectance comparative study of benzil inclusion within microcrystalline cellulose and β-cyclodextrin

Luis F. Vieira Ferreira,*[a] Isabel Ferreira Machado,[a] José P. Da Silva[a,b] and Anabela S. Oliveira[a]

[a] *Centro de Química-Física Molecular – Complexo Interdisciplinar, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

[b] *FCT, Universidade do Algarve, Campus de Gambelas, 8005-139 Faro, Portugal*

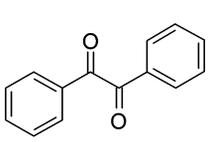
Received 14th July 2003, Accepted 8th September 2003
First published as an Advance Article on the web 24th September 2003

Diffuse reflectance and laser-induced techniques were used to study photochemical and photophysical processes of benzil adsorbed on two solid powdered supports, microcrystalline cellulose and β-cyclodextrin. In both substrates, a distribution of ground-state benzil conformers exists, largely dominated by skew conformations where the carbonyl groups are twisted one to the other. Room temperature phosphorescence was observed in air-equilibrated samples in both cases. The decay times vary greatly and the largest lifetime was obtained for benzil/β-cyclodextrin, showing that this host's cavity accommodates benzil well, enhancing its room temperature phosphorescence. Triplet–triplet absorption of benzil entrapped in cellulose was detected and benzil ketyl radical formation also occurred. With benzil included into β-cyclodextrin, and following laser excitation, benzoyl radicals were detected on the millisecond timescale. Product analysis and identification of laser-irradiated benzil samples in the two hosts clearly showed that the main degradation photoproducts were benzoic acid and benzaldehyde. The main differences were a larger benzoic acid/benzaldehyde ratio in the case of cellulose and the formation of benzyl alcohol in this support.

1 Introduction

Time-resolved laser-induced luminescence, diffuse reflectance laser flash photolysis and ground-state diffuse reflectance absorption spectroscopy are relatively new techniques that can be applied to study opaque and crystalline systems.[1–3] These solid-state photochemical methods have been recently applied by our group to study several organic compounds adsorbed onto different hosts, including *p-tert*-butylcalix[4]-, -[6]- and -[8]arenes,[3] microcrystalline cellulose,[4] silicalite and cyclodextrins,[5] and silica,[6] amongst others. The properties and applications of such solid substrates are described elsewhere.[1]

Benzil is an α-dicarbonyl compound and presents different conformations due to rotation of the central carbonyl–carbonyl bond in the ground and excited states[7–10] (Scheme 1). In the ground state, it has a non-planar (skew) conformation, the twist angle of the two benzoyl moieties being about 72°. Upon excitation in fluid media, both the first excited singlet state and the first excited triplet state relax to an identical conformation, *i.e.* to an *s-trans* planar geometry in which the Ph–C(O)–C(O)–Ph dihedral angle is 180°.[8,10] Therefore, both fluorescence and phosphorescence are dependent on external constraints imposed by the environment. Benzil has an n ⟶ π* absorption transition and was found to have zero or near zero dipole moment in the triplet state in benzene solution, thus confirming the *s-trans* structure of the excited state.[10] Benzoyl and benzil ketyl radicals were detected in solution flash photolysis[8a,c,11,12] and time-resolved electron spin resonance studies.[13]



Benzil (BZL)

Scheme 1

Microcrystalline cellulose is a very useful powdered solid support due to its remarkable property of protecting adsorbed probes from oxygen action.[1,4] Adsorption of probes on microcrystalline cellulose can be achieved by the use of a solution of the probe (benzil) in polar protic (*e.g.* alcohols) or aprotic (*e.g.* acetonitrile, acetone, dioxane) solvents. When the solid substrate is added to this solution, cellulose–cellulose hydrogen bonds are replaced by cellulose–solvent bonds and the matrix exhibits a certain degree of swelling, which depends on the solvent used for sample preparation.[4] Probes can then penetrate within the polymer chains and remain entrapped after solvent removal.

Cyclodextrins are naturally occurring oligosaccharides produced by enzymatic degradation of starch. They are composed of six (α-CD), seven (β-CD), eight (γ-CD), or more glucose units joined by α-(1,4) linkages.[14,15] They have a rigid torus-shaped hydrophobic cavity, with variable cavity diameter (5.6 Å for α-CD, 6.8 Å for β-CD and 8.0 Å for γ-CD), and are able to include a great variety of organic, inorganic, neutral and ionic molecules[14,15] in their intramolecular cavities, depending on the size and geometry of the guest molecule, and also on the host cavity. Cyclodextrins are used in several industrial processes in the pharmaceutical, food and chemical industries.[14a]

Following a previous study of benzil included into *p-tert*-butylcalix[*n*]arenes (*n* = 4, 6 and 8),[3a] we have inserted the same probe into two new hosts. In this paper, we present a diffuse reflectance, laser-induced luminescence and chromatographic study of benzil entrapped in microcrystalline cellulose polymer chains. These results will be compared with those obtained with another electronically inert host, β-cyclodextrin, where benzil is included into its relatively non-polar cavity. We will show that in these two different solid powdered supports, this α-diketone exhibits distinct photochemical behaviour. The obtained results enable us to propose reaction mechanisms for benzil in both supports.

2 Experimental

Materials

Microcrystalline cellulose (Fluka DS0, average particle size 50 μm) and β-cyclodextrin (Aldrich) were used without further purification. Benzil (Aldrich) was recrystallised from ethanol.

DOI: 10.1039/b307956b

The solvents, methanol, dichloromethane, diethyl ether and ethanol (Merck, Uvasol grade), were used as received. Benzoin, benzhydrol, benzoic acid, benzyl alcohol and benzaldehyde were from Aldrich, biphenyl from Eastman-Kodak (highest purity available) and benzophenone from Koch-Light (scintillation grade).

Sample preparation

The microcrystalline cellulose samples used in this work were prepared using the solvent evaporation method. This method involves addition of a solution containing the probe to the powdered solid substrate (previously dried under vacuum, *ca.* 10^{-3} mbar, at 60 °C for 24 h), after covering the powdered support with ethanol, a solvent which efficiently swells the substrate. The resulting mixture was magnetically stirred for at least 24 h, allowing the probe to penetrate within the natural polymer chains. Finally, solvent evaporation was performed by placing the stirred slurry in a fume cupboard.

The final solvent removal was performed overnight in an acrylic chamber with an electrically heated shelf (Heto FD 1.0–110) with temperature control (30 ± 1 °C), again under a moderate vacuum. The existence of final traces of solvent was monitored by FTIR spectroscopy.

In these samples, the total amount of benzil per solid sample is controlled and the exact concentration of the ketone per gram of support is known.

Portions of these samples were weighed and then carefully washed with a solvent which does not swell cellulose, in this case dichloromethane (10 ml of solvent, 5 times, 2 ml aliquots per gram of sample). In this way, non-entrapped benzil was removed from the cellulose surface. The concentration of the ketone per gram of support in the samples was calculated using ground-state diffuse reflectance absorption spectroscopy, involving measuring the remission functions of 'washed' samples and comparing them with those of 'unwashed' samples where the exact concentration of the ketone per gram of cellulose is known.

The benzil/β-CD samples were prepared by adding to a saturated solution of β-CD in water a saturated solution of benzil in methanol. The resulting mixture was magnetically stirred for 48 h and then lyophilised. The powdered solid complex was then washed with 10 ml of diethyl ether (5 times, 2 ml aliquots per gram of sample) to remove all non-complexed benzil and, finally, the samples were dried under reduced pressure. The drying procedure was the same as for the cellulose samples.

Methods

Ground-state diffuse reflectance absorption spectra (GSDR). Ground-state absorption spectra for the solid samples were recorded using an OLIS 14 spectrophotometer with a diffuse reflectance attachment. Further details are given elsewhere.[1,3,4]

Diffuse reflectance laser flash photolysis (DRLFP) and laser-induced luminescence (LIL). Schematic diagrams of the DRLFP and LIL systems are presented in recent reports.[1,5b] Laser flash photolysis experiments were carried out with the second or third harmonics of a Nd:YAG laser (355 and 266 nm, *ca.* 6 ns FWHM, ~10–30 mJ pulse^{-1}) from B. M. Industries (Thomson-CSF Saga 12–10), in the diffuse reflectance mode.[1,3] The light arising from the irradiation of solid samples by the laser pulse was collected by a collimating beam probe coupled to an optical fibre (fused silica) and detected by a gated intensified charge-coupled device (Andor ICCD detector, based on the Hamamatsu S5769–0907). The ICCD was coupled to a fixed imaging compact spectrograph (Oriel FICS 77440). The system can be used either by capturing all light emitted by the sample or in a time-resolved mode by using a delay box (Stanford Research Systems D6535). The ICCD has high speed gating electronics (2.2 ns) and intensifier and covers the 200–900 nm wavelength range. Time-resolved absorption and emission spectra are available in the nanosecond to second time range.[1,3] Transient absorption data are reported as percentage of absorption (%Abs.), defined as $100\Delta J_t/J_0=(1 - J_t/J_0)100$, where J_0 and J_t are the diffuse reflected light from the sample before exposure to the exciting laser pulse and at time t after excitation, respectively.[1,3]

For the laser-induced luminescence experiments, a N_2 laser (PTI 2000, *ca.* 600 ps FWHM, ~1.0 mJ pulse^{-1}) was also used.

Irradiation and product analysis. Photodegradation studies under lamp irradiation were conducted in a reactor previously used to study the photochemistry of pesticides.[5a] The samples were irradiated at 254 nm using a 16 W low pressure mercury lamp (Applied Photophysics) without filters and without refrigeration. Laser irradiation at 355 nm was also used. The degradation products were analysed after extraction with acetonitrile (a known weight of sample in a known volume of solvent), followed by centrifugation. Extractions with methanol were also performed. Photolysis was followed by HPLC using a Merck-Hitachi 655A-11 chromatograph equipped with 655A-22 UV and Shimadzu SPD-M6A photodiode array detectors. A Merck LiChroCART 125 (RP-18, 5 μm) column was employed and the runs were performed using water–acetonitrile mixtures. The extracts were also analysed by GC-MS using a Hewlett Packard 5890 Series II gas chromatograph with a 5971 series mass-selective detector (EI 70 eV). A Chrompack CP-WAX 58CB capillary column 25 m in length and with 0.25 mm I.D. and a DB-1 capillary column 30 m in length and with 0.25 mm I.D. (J & W Scientific) were used. The initial temperature of 70 °C was maintained for 5 min and then increased at a rate of 5 °C min^{-1} up to 250 °C.

3 Results and discussion

Ground-state diffuse reflectance absorption spectra

Fig. 1(a) shows the ground-state electronic absorption spectra of samples of benzil/cellulose for three probe loadings (100, 250 and 500 μmol of probe per gram of support), n ⟶ π* transition only, with absorption maxima around 384 nm. The ground-state absorption spectrum of the pure powdered cellulose support is also shown (trace 1). The data are presented as the remission function, $F(R)$, where $F(R) = (1 - R)^2/2R$ and R is the reflectance at the excitation wavelength, as a function of wavelength. The inset shows $F(R)$ as a linear function of the concentration, and also that the maximum absorption wavelength is constant within experimental error.

Fig. 1(b) compares the spectrum of a 'washed' sample of benzil/cellulose with that of an 'unwashed' sample. As described in the sample preparation section, dichloromethane is a non-swelling solvent towards microcrystalline cellulose. Thus, washing with dichloromethane means that all benzil molecules which are not entrapped within cellulose polymeric chains or strongly attached to the cellulose surface are removed from the sample, including any microcrystals of benzil which may be deposited on the surface. The n ⟶ π* absorption region of benzil does not present a clear vibronic structure, but rather a non-structured and broad absorption band. This broadening effect increases in the 'washed' sample, suggesting a larger number of different ground-state conformers of benzil in this case, namely those approaching planarity which absorb at longer wavelengths. At the same time, the absorption maximum deviates from 384 nm for the 'unwashed' sample to about 375 nm for the 'washed' sample, in accordance with an increase in the polarity of the host similar to that reported in ref. 3*a* (n ⟶ π* transition deviates to the blue with increasing polarity). This observation reflects the close contact of benzil with the cellulose polymer chains, which have hydroxyl groups and an oxygen atom per glucose ring, and hence provide a polar environment.

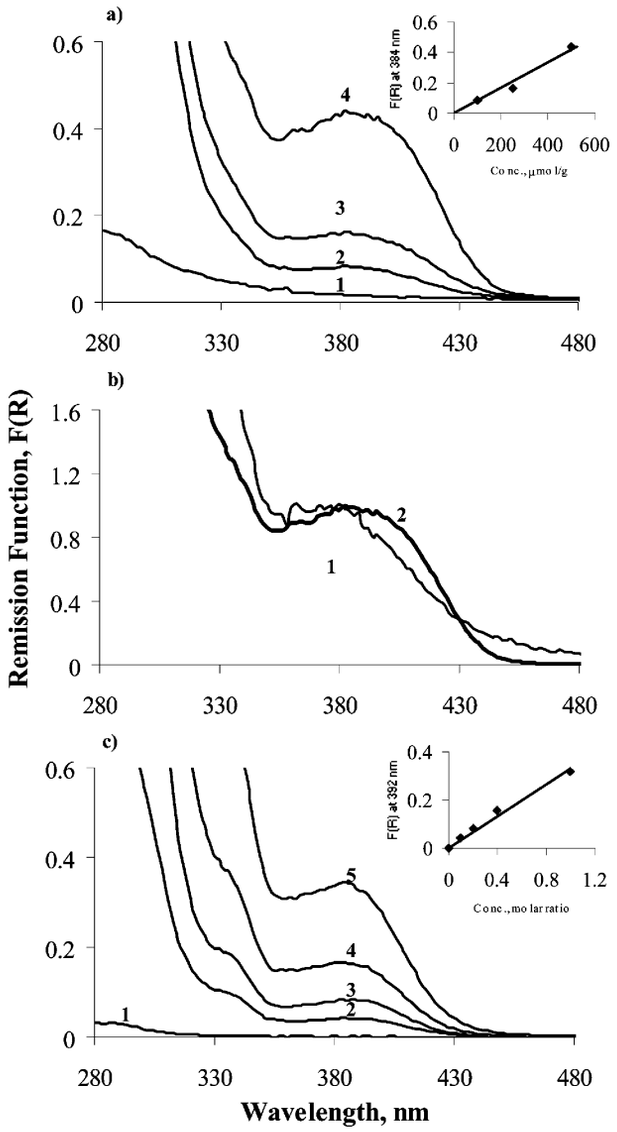


Fig. 1 (a) Remission functions for benzil/cellulose samples prepared using ethanol as the swelling agent. Trace 1 is for the substrate alone and traces 2, 3 and 4 are for 'unwashed' samples containing 100, 250 and 500 μmol of benzil per gram of cellulose, respectively. (b) Remission functions for benzil/cellulose samples with an initial benzil concentration of 500 μmol g(cellulose)$^{-1}$. Trace 1 is for the 'washed' sample and trace 2 for the 'unwashed' sample. The remission function traces are normalised to unity at 380 nm. (c) Remission functions for benzil/β-cyclodextrin samples with 1 : 10, 1 : 5, 1 : 2.5 and 1 : 1 guest : host molar ratios (traces 2, 3, 4 and 5 respectively), and also for the substrate alone (trace 1).

The use of the *F*(*R*) *versus* concentration plot shown in the inset of Fig. 1(a) enabled us to calculate that only about 20% of the benzil molecules stayed entrapped in the cellulose polymer chains after washing with choroform.

Fig. 1(c) shows the remission function spectra obtained for 1 : 10, 1 : 5, 1 : 2.5 and 1 : 1 molar ratio samples of benzil included into β-cyclodextrin, as well as the absorption of the substrate alone over the same wavelength range (trace 1). As described previously, this host has a torus-shaped internal cavity which probes may enter, and with a certain hydrophobic character.[15] The absorption spectra are not too different from those obtained for the cellulose samples, peaking now at 392 nm, in accordance with a less polar environment. The intramolecular dimensions of β-cyclodextrin are large enough for benzil to enter these cavities with no imposition of severe conformational restrictions. In another case (silicalite hydrophobic channels) benzil molecules are forced to assume an *s-trans* planar conformation, even in the ground state.[3a]

Room temperature laser-induced luminescence

Fig. 2(a) shows the room temperature phosphorescence spectra of an air-equilibrated 500 μmol g(cellulose)$^{-1}$ benzil/cellulose sample prepared using ethanol as the solvent, while Fig. 2(b) presents similar data obtained after washing the sample with dichloromethane. We used a short pulse from a nitrogen laser at 337 nm (600 ps FWHM, ~1.0 mJ pulse^{-1}) as the excitation source, which is suitable for benzil time-resolved luminescence studies due to its short duration.

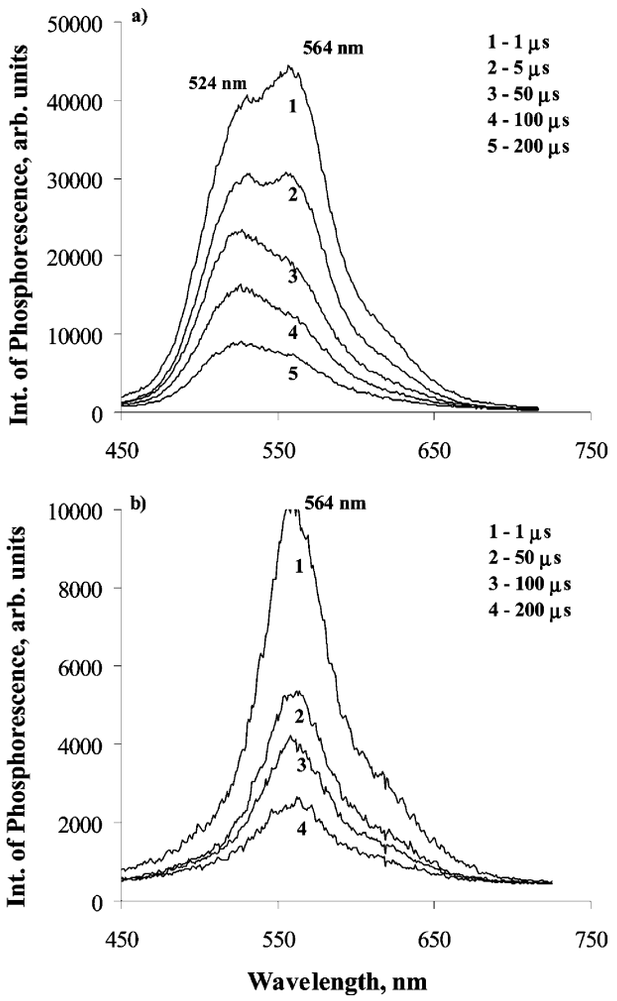


Fig. 2 Room temperature laser-induced phosphorescence emission spectra from (a) an air-equilibrated 'unwashed' 500 μmol g(cellulose)$^{-1}$ benzil/cellulose sample and (b) a 'washed' benzil/cellulose sample with the same initial benzil concentration.

Remarkable differences can be seen in the room temperature phosphorescence spectra of 'unwashed' and 'washed' samples. In the former case, trace 1, obtained 1 μs after the laser pulse, shows two maxima at 524 and 564 nm. The species responsible for the emission at 564 nm decays faster than the species responsible for the 524 nm emission, and in trace 5 (obtained 200 μs after the laser pulse), the predominant emission is the latter one.

These time-resolved phosphorescence spectra were compared with others obtained from samples of benzil on cellulose, but prepared using dichloromethane as the solvent (data not shown), and also from mechanical mixtures of benzil and cellulose containing the same amount of benzil per gram of cellulose (data also not shown). Dichloromethane is a non-swelling solvent for cellulose and the probe does not penetrate into the polymer chains of the solid support. For this reason, a 524 nm emission, characteristic of benzil microcrystals, is observed for this sample. Similarly, the same emission is also observed for the mechanical mixture.[3a,16]

Some of the benzil molecules are not included into the microcrystalline cellulose, rather, they are deposited on the surface of the powdered solid support in the form of microcrystals. These molecules emit from an unrelaxed conformation, the phosphorescence peaking at 524 nm. The entrapped benzil molecules emit from relaxed conformations, *i.e.* inside the cellulose, benzil has enough space to rotate axially and assume *s-trans* conformations, which emit at longer wavelengths, the maximum emission peaking at 564 nm. This emission, however, is not the predominant one in these 'unwashed' samples.

This effect has been well described in solution studies of benzil.[7,8] The room temperature and low temperature (77 K) solution emission spectra of benzil correspond to 'relaxed' and 'unrelaxed' excited states of this probe, respectively. The relaxed excited state has an *s-trans* planar geometry with zero dipole moment,[10] while the 'unrelaxed' form corresponds to a skew conformation, both in the singlet and triplet states. As a consequence, the phosphorescence emission maxima from *s-trans* planar conformers are shifted about 40 nm to the red in comparison to those from the skew conformers.[7,8] Another consequence of this extensive conformational reorganisation upon excitation is that while ground-state benzil molecules exhibit a dipole moment of 3.75 D, in the excited state, the dipole moment is zero.[10]

Lifetimes were determined for air-equilibrated and argon-purged samples. Taking into account the longer component of the decay only, values of 115 and 155 μs, respectively, were obtained for 'unwashed' samples, showing that some of the benzil on the surface can be reached by oxygen, which quenches the excited triplet state of benzil.

For 'washed' samples of benzil/cellulose, a different situation was found, as Fig. 2(b) shows. As stated before, only the benzil molecules entrapped within or strongly bound to the polymer chains stay in the sample (about 20% of the initial benzil), and they phosphoresce predominantly from *s-trans* conformers, the emission peaking at 564 nm. This phosphorescence emission is the same in both air-equilibrated and argon-purged samples, and the lifetime determined for the longer component of the decay is about 180 μs.

Fig. 3(a) shows the phosphorescence emission spectra of inclusion complexes of benzil/β-cyclodextrin, with a long-lived emission of benzil (lifetime about 275 μs). The same lifetimes were obtained for air-equilibrated and argon-purged samples, showing that the β-cyclodextrin cavity protects benzil from being quenched by oxygen. The fact that for benzil/β-cyclodextrin samples the phosphorescence emission peaks at 572 nm, *i.e.* it originates from a relaxed form, while for benzil microcrystals the emission peaks at 524 nm is a clear indication of inclusion of benzil into the β-cyclodextrin cavity.

Apart from the phosphorescence emission, fluorescence emission was also detected, with lifetimes around 2 ns, in accordance with the value previously reported for this prompt emission.[3a,9] Fig. 3(b) presents this fluorescence emission for benzil within β-cyclodextrin, superimposed on the much longer-lived phosphorescence emission with a maximum at about 572 nm. To obtain these time-resolved fluorescence spectra, we simply used a nanosecond time gate in our intensified charge-coupled device, triggering the detector immediately after the laser pulse rather than introducing a delay after the pulse, to separate the long-lived emissions from the prompt ones. Finally, Fig. 3(a) shows the existence of some delayed fluorescence with emission maxima at about 505 nm, which is significant in the case of benzil/β-cyclodextrin.

The important facts to keep in mind from these luminescence studies are the following: in microcrystalline cellulose, benzil may be entrapped within the polymer chains and protected from oxygen action; this is the case for 'washed' samples and possibly in a mixed situation (entrapped and in the form of surface microcrystals) in 'unwashed' samples. In contrast, in β-cyclodextrin, benzil is included into the hydrophobic cavity,

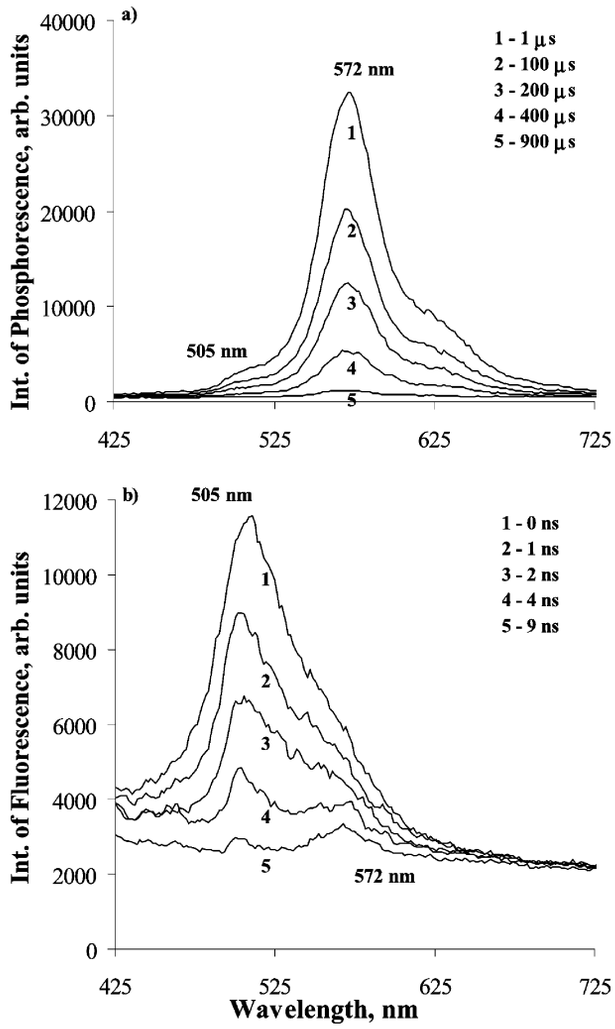


Fig. 3 Room temperature laser-induced luminescence spectra from an air-equilibrated sample of the benzil/β-cyclodextrin inclusion complex (molar ratio 1 : 1): (a) time-resolved phosphorescence emission spectra; (b) time-resolved fluorescence emission spectra.

well protected from oxygen action. These experimental observations are important, together with transient absorption data, to gain an understanding of the photochemistry of benzil on these two different supports.

Diffuse reflectance laser flash photolysis

Time-resolved absorption spectra of samples of 'unwashed' and 'washed' benzil/cellulose samples and of benzil/β-cyclodextrin samples were obtained using the diffuse reflectance laser flash photolysis technique, developed by Wilkinson and co-workers.[2] In this study, the use of an intensified charged-coupled device as the detector allowed us to obtain time-resolved absorption spectra with nanometer spectral resolution.[1,3]

Fig. 4(a) and (b) show the time-resolved absorption spectra of benzil/cellulose (with ethanol as the solvent for sample preparation) for 'unwashed' and 'washed' samples, respectively. Fig. 4(c) shows spectra for a mechanical mixture of benzil and cellulose with the same benzil concentration as in the 'unwashed' sample (500 μmol g^{-1}). Fig. 5 shows similar data for the benzil/β-cyclodextrin guest/host system. All spectra were obtained for air-equilibrated samples, exciting at 355 nm.

Transient absorption spectra of 'unwashed' benzil/cellulose samples provide clear evidence for the formation of triplet benzil and also of the ketyl radical of benzil. The triplet–triplet absorption spectra of entrapped benzil peaks at about 480 nm and the triplet excited species has a lifetime on the timescale of

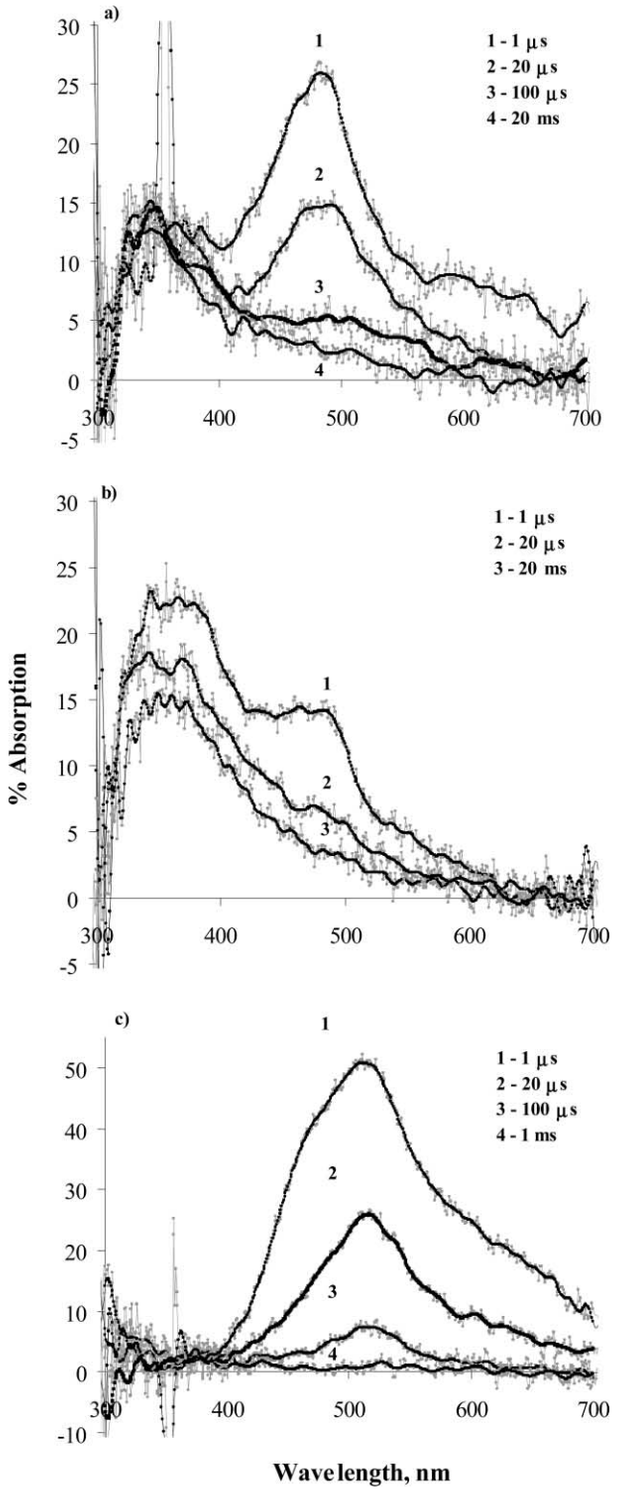


Fig. 4 Time-resolved absorption spectra for (a) an 'unwashed' 500 μmol g(cellulose)$^{-1}$ benzil/cellulose sample prepared using ethanol as the swelling agent, (b) a benzil/cellulose sample with an initial benzil concentration of 500 μmol g(cellulose)$^{-1}$ after washing with dichloromethane and (c) a mechanical mixture of benzil and microcrystalline cellulose containing 500 μmol of benzil per gram of cellulose. All samples were air-equilibrated, λ_{exc} = 355 nm in all cases.

about 100 μs, and can be still observed in trace 3 of Fig. 4(a). However, at longer times (trace 4 is 20 ms after the laser pulse), only the ketyl radical transient absorption of benzil can be seen. The triplet–triplet absorption spectrum of benzil adsorbed onto the cellulose surface was easily identified by comparison with previous work on surfaces covered with microcrystals of benzil,[16] benzil within calixarenes[3a] and also solutions of benzil.[8c,11a,12] The ketyl radical of benzil was identified by comparison with previous data reported for benzil and

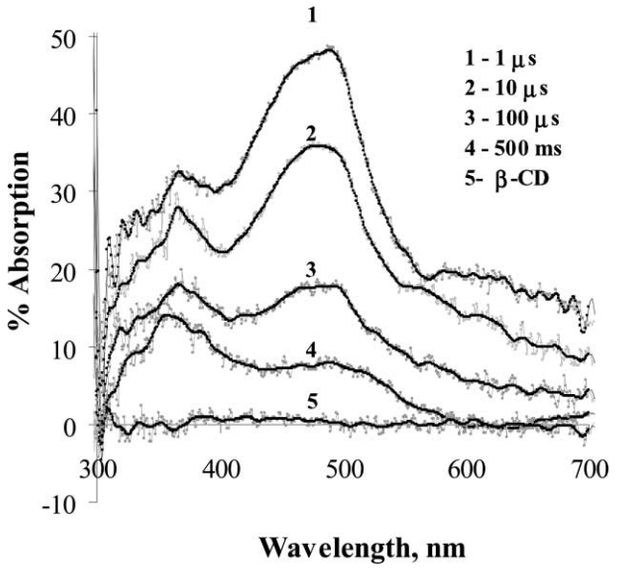


Fig. 5 Time-resolved absorption spectra for a benzil/β-cyclodextrin sample with a 1 : 1 guest : host molar ratio. (λ_{exc} = 355 nm).

triethylamine in benzene,[9] benzil in propanol[13] and other mixtures.[12a] The spectrum of the ketyl radical of benzil peaks at about 360 nm and the molar absorption coefficient was reported to be quite high (ε = 8800 L mol^{-1} cm^{-1} in acetonitrile).[17b] It is important to note that benzoyl radicals may also be formed in this case, resulting from α-cleavage of entrapped benzil. The molar absorption coefficient reported for benzoyl at about 360 nm is quite small (ε = 150 L mol^{-1} cm^{-1} in acetonitrile)[17b] when compared with that of the benzil ketyl radical, and this obviously means that the transient species may also be there, but that its transient absorption is masked by the much stronger transient absorption of the benzil ketyl radical.

The major difference between the transient absorption spectra of 'washed' and 'unwashed' benzil/cellulose samples is that in the former, triplet–triplet absorption is reduced, while ketyl radical formation is increased to a remarkable degree. Only well-entrapped benzil molecules stay adsorbed within the polymer chains and the remaining benzil molecules are in close contact with cellulose. As a consequence, intermolecular hydrogen atom abstraction predominates in these samples.

The spectra shown in Fig. 4(c) for a mechanical mixture of benzil and cellulose only exhibits the transient triplet–triplet absorption of this α-diketone. It is interesting to note that triplet–triplet absorption of microcrystals of benzil peak at about 510 nm, while when adsorbed on cellulose, the triplet–triplet absorption of benzil peaks at about 480 nm. This reflects the existence of more planar conformers in the case of adsorption on cellulose and puckered conformers in the microcrystals.[8c] In Fig. 4(c), a small shoulder can be seen at *ca.* 460 nm in trace 1 (1 μs after laser pulse) which is apparently absent in the 20 μs trace. No special kinetic features were detected at this wavelength. This is simply a consequence of the large emission correction necessary for this short timescale, which then decreases for longer timescales. Some reduced adsorption could have taken place in the mechanical mixture of benzil and microcrystalline cellulose; however, Fig. 4(c) shows no significant absorption attributable to the benzil ketyl radical.

The triplet–triplet transient absorption of benzil can be seen in Fig. 5 (benzil/β-cyclodextrin inclusion complex, 1 : 1 molar ratio) in the microsecond time range, while the benzoyl radical absorption becomes evident in the millisecond/second time range. In these spectra, the new species appears and becomes more evident at much longer times (500 ms after laser pulse), the absorption peaks at about 360 nm with a shoulder at about 480 nm, characteristic of the benzoyl radical absorption.[17,18]

No benzil ketyl radicals were formed in the β-cyclodextrin samples following the laser pulse. If some ketyl radicals had been formed, they should certainly have been detected in the time-resolved spectra due to the high molar absorption coefficient of this species, and their transient absorption would completely mask that at 480 nm due to the benzoyl radical. The absence of ketyl radical formation is probably related to the fact that, due to the reduced internal space of the β-cyclodextrin cavity, no suitable conformation for the hydrogen abstraction reaction occurs. So we see either the triplet excited state of benzil or the radicals that are derived from the α-cleavage reaction, *i.e.* benzoyl radicals.

Further studies of the photodegradation of benzil support these assignments, as we will see in the next section.

Photodegradation products studies

The solution photochemistry of benzil has been studied by flash photolysis and mainly reported by Scaiano *et al.*[11] The reactions involved can be briefly described by the following:

$$\mathrm{Ph{-}C(O){-}C(O){-}Ph} \xrightarrow{h\nu} {}^{1}\{\mathrm{Ph{-}C(O){-}C(O){-}Ph}\}^{*} \quad (1)$$

$${}^{1}\{\mathrm{Ph{-}C(O){-}C(O){-}Ph}\}^{*} \longrightarrow {}^{3}\{\mathrm{Ph{-}C(O){-}C(O){-}Ph}\}^{*} \quad (2)$$

$${}^{3}\{\mathrm{Ph{-}C(O){-}C(O){-}Ph}\}^{*} \longrightarrow 2\ \mathrm{Ph{-}C^{\bullet}O} \quad (3)$$

$${}^{3}\{\mathrm{Ph{-}C(O){-}C(O){-}Ph}\}^{*} \xrightarrow{+\mathrm{H}^{\bullet}} \mathrm{Ph{-}C^{\bullet}(OH){-}C(O){-}Ph} \quad (4)$$

Reaction 3 describes the formation of the benzoyl radical (Norrish type I cleavage) following laser excitation, and reaction 4 the formation of the benzil ketyl radical (intermolecular hydrogen atom abstraction).[11] Photoreduction of benzil originates, in general, benzil ketyl radicals in non-polar solvents and the radical anion in hydroxylic media.[11c] This latter species is easily identified since its transient absorption peaks at about 600 nm,[11b] so we can be confident that the radical anion is not formed in our cases.

One can expect reactions 3 and 4 to occur in the reverse direction, with the re-formation of the starting materials or subsequent second hydrogen atom abstraction, yielding benzaldehyde and benzoin, respectively.

Following laser excitation (355 nm) or lamp irradiation (254 nm) product analysis and identification was attempted. In the case of the β-cyclodextrin samples, the main degradation products are benzaldehyde and benzoic acid. The former has previously been reported as resulting from the photodegradation of benzil in solution and on solid supports.[12a,17b,19] The same main degradation products were detected on 'unwashed' cellulose but the benzoic acid/benzaldehyde ratio is about one order of magnitude higher than is observed for benzil inclusion in β-cyclodextrin. Benzaldehyde is easily accounted for by the formation of the benzoyl radical, which is the dominant transient in the β-cyclodextrin samples and can lead to benzaldehyde by hydrogen abstraction. This result indicates that, unlike benzil triplets, benzoyl radicals are able to abstract hydrogen atoms in this support. This behaviour probably reflects the fact that their smaller size enables them to move in order to abstract hydrogen atoms from the end of the torus-shaped β-cyclodextrin cavity. Benzoic acid was reported as resulting from the photodegradation of benzil in solution and in polymer systems, and its formation involves molecular oxygen.[12a,17a,19,20] However little oxygen effect is expected in the supports under study since both are able to protect the adsorbed probes, to a certain degree, from the action of molecular oxygen[4,5b] in the air. Therefore, the role of oxygen in benzoic acid formation from benzil in cellulose and β-cyclodextrin was studied in detail.

The larger benzoic acid/benzaldehyde ratio observed on 'unwashed' cellulose gives the first indication of the role of

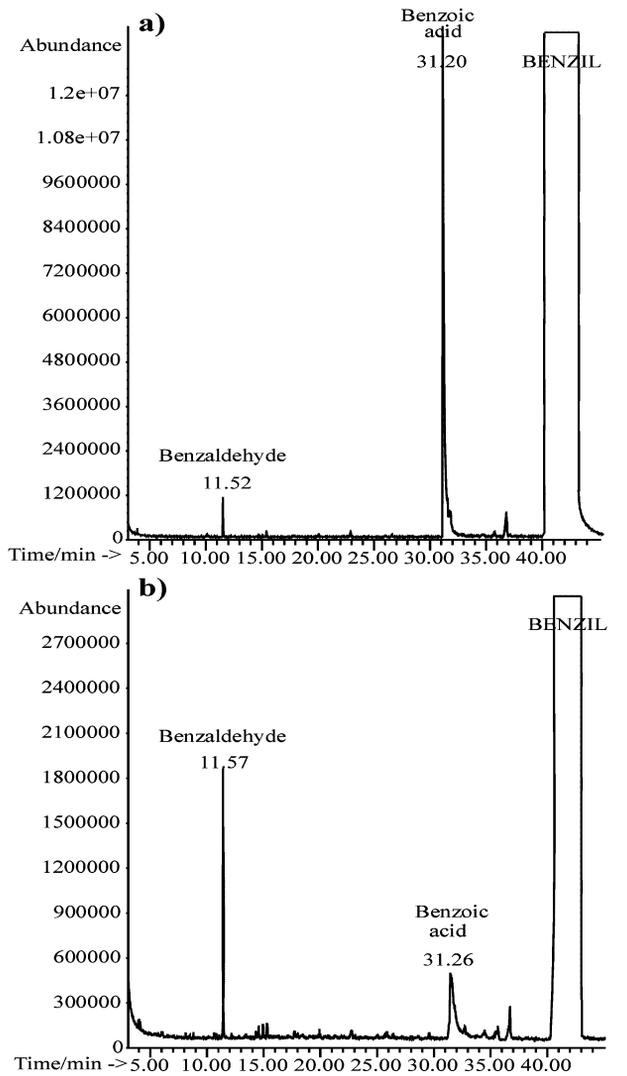
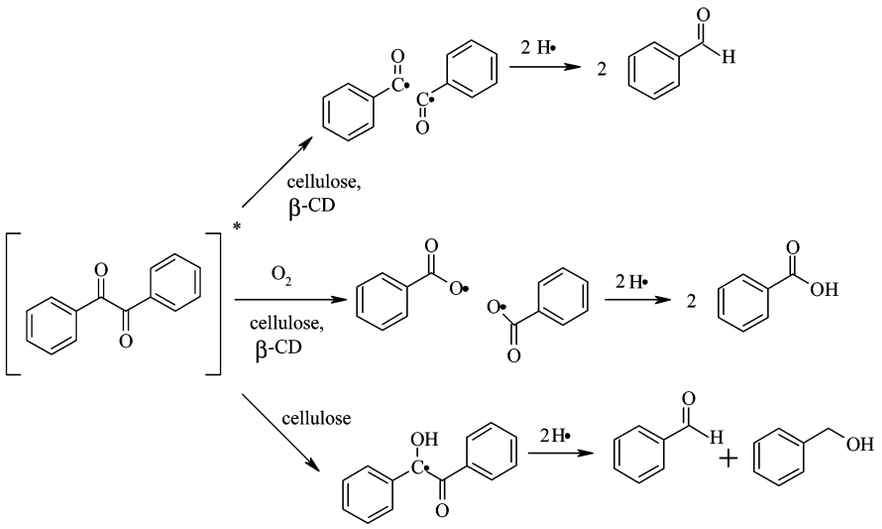


Fig. 6 GC-MS chromatograms of the acetonitrile extract from an 'unwashed' laser-irradiated sample of benzil/cellulose: (a) air-equilibrated; (b) argon-purged.

oxygen in the formation of benzoic acid. Fig. 6(a) shows a typical GC-MS chromatogram of the extract (in acetonitrile) of an 'unwashed' benzil/cellulose sample and indicates that benzoic acid is the main degradation product. This result is attributed to surface-bound benzil molecules, which are not protected from oxygen action by the polymer and are therefore more accessible to bombardment from the gas phase. This effect is consistent with the observed quenching effect in the phosphorescence of air-equilibrated samples. The analysis of irradiated 'washed' samples indicated that the benzoic acid/benzaldehyde ratio decreased about five times relative to the 'unwashed' samples (results not shown). The washing procedure removes mainly the surface-bound benzil, leaving just the well-entrapped molecules, which are less accessible to oxygen. Therefore, the formation of benzoic acid must involve molecular oxygen at some stage of the reaction process.

'Unwashed' and 'washed' samples were also irradiated under an argon atmosphere, *i.e.* after purging the samples with argon for about 10 min. The results indicate an approximately five-fold decrease in the benzoic acid/benzaldehyde ratio for the 'washed' sample and 20-fold for 'unwashed' cellulose, relative to the air-equilibrated samples [compare Fig. 6(a) and (b) for the 'unwashed' case]. The chromatographic results also give a similar ratio for both the 'washed' and 'unwashed' samples. This result confirms that molecular oxygen plays a pivotal role in the benzoic acid formation and also verifies that the interaction of the surface-bound benzil molecules in the 'unwashed'



Scheme 2

sample are responsible for the strong oxygen effect. The formation of benzoic acid in β-cyclodextrin and in the 'washed' cellulose samples is related to the oxygen already trapped in the solid sample. Methyl benzoate was detected in all samples when the extraction was carried out using methanol, as has been observed in the photochemistry of benzil/calix[*n*]arene (*n* = 4, 6 and 8) complexes.[3a]. Other identified photoproducts were benzophenone, 2-hydroxybenzophenone, phenylbenzoate, benzyl alcohol and biphenyl. Most of these products can be accounted for by benzoyl radical reactions (decarbonylation and radical coupling) and/or photodegradation of the primary degradation products of benzil. All identifications were based on the analysis of authentic samples and/or GC-MS data.

With the methodology used in this work and described in the Experimental section, only the photoproducts extracted with acetonitrile could be chromatographically detected. Therefore, we do not exclude the formation of addition products of radicals (ketone derivatives) formed from hydrogen abstraction and the β-cyclodextrin macrocycle, as described in the literature for similar cases.[21,22]

Scheme 2 summarises the main photoreaction pathways of benzil on cellulose and β-cyclodextrin. The α-cleavage of benzil is one of the main reaction pathways in both supports and, as observed in calixarenes,[3a] can occur upon laser excitation or lamp irradiation, the latter suggesting that the reaction may occur by a monophotonic process. Benzaldehyde is the major degradation product on β-cyclodextrin. This result is in agreement with the transient absorption data, since benzoyl radicals can lead to benzaldehyde by hydrogen abstraction and this radical is the main transient in β-cyclodextrin. Two pathways have been proposed for the formation of benzoic acid by photodegradation of benzil in solution and in polymeric systems.[12,20] One involves the direct reaction of molecular oxygen with triplet benzil, resulting in formation benzoyl peroxide, which leads to benzoic acid by hydrogen abstraction. The other pathway involves the formation of benzoyl peroxyl radicals through the reaction of benzoyl radicals and molecular oxygen. Both pathways can occur in the supports studied herein, the former being dominant in the 'unwashed' cellulose samples. We believe the latter mechanism to be less important in our case, due to the fact that we have a rigid environment with reduced mobility for the acylperoxyl radicals to couple. Aside from this, the mechanism involves two oxygen molecules and is therefore less likely to occur in solid supports.

The benzil ketyl radical is the main transient on cellulose. This is a result of the highly reducing environment provided by cellulose, which suggests benzoin formation might be a possibility.[3a] However, this compound was not detected, even in trace amounts, in any of the analysed extracts. It is well known from the literature that benzoin undergoes a fast photodegradation reaction, leading to benzaldehyde and benzyl alcohol as the main degradation products.[19,23,24] The latter product was indeed detected on cellulose, suggesting a relation between ketyl radicals and benzyl alcohol formation.

4 Conclusions

Inclusion of benzil into different hosts, namely microcrystalline cellulose and β-cyclodextrin, results in significant changes both in ground-state absorption spectra as well as time-resolved emission and absorption spectra.

When the host is microcrystalline cellulose and the samples are 'unwashed', the benzil molecules stay deposited on the surface as well as entrapped within the natural polymer chains. Apart from triplet formation, hydrogen abstraction also occurs, the latter reaction being predominant in 'washed' cellulose samples.

In the case of β-cyclodextrin as host, benzil is in a hydrophobic and more constrained environment, and only the transient absorption of the benzoyl radical was detected (apart from the triplet–triplet absorption of benzil).

Product analysis and identification of laser-irradiated samples of benzil in both hosts clearly showed that the main degradation photoproducts detected were benzoic acid and benzaldehyde. The main differences are a larger benzoic acid/benzaldehyde ratio on cellulose and the formation of benzyl alcohol in this support.

Acknowledgment

A. S. O. and J. P. S. thank FCT for Post-Doctoral Fellowships SFRH/BPD/36500/2000 and SFRH/BPD/15589/2001.

References

1 (*a*) L. F. Vieira Ferreira, Fotoquímica de corantes e outras moléculas orgânicas em superfícies, *Química*, 1999, **72**, 28–46; (*b*) A. M. Botelho do Rego and L. F. Vieira Ferreira, in *Handbook of Surfaces and Interfaces of Materials*, ed. H. S. Nalwa, Academic Press, New York, 2001, vol. 2, ch. 7, pp. 275–313.

2 (*a*) F. Wilkinson and G. P. Kelly, in *Photochemistry on Solid Surfaces*, ed. M. Anpo and T. Matsuara, Elsevier, Amsterdam, 1989, pp. 31–47; (*b*) F. Wilkinson and G. P. Kelly, in *Handbook of Organic Photochemistry*, ed. J. C. Scaiano, CRC Press, Boca Raton, 1989, vol. 1, ch. 12, pp. 293–314.

3 (*a*) L. F. Vieira Ferreira, I. Ferreira Machado, A. S. Oliveira, M. R. Vieira Ferreira, J. P. Da Silva and J. C. Moreira, A diffuse reflectance comparative study of benzil inclusion within *p-tert*-butylcalix[*n*]arenes (*n* = 4, 6 and 8) and silicalite, *J. Phys. Chem. B*, 2002, **106**, 12 584–12 593; (*b*) L. F. Vieira Ferreira, M. R. Vieira Ferreira, A. S.

Oliveira and J. C. Moreira, Potentialities of diffuse reflectance laser-induced techniques in solid phase: a comparative study of benzophenone inclusion within *p-tert*-butylcalixarenes, silicalite and microcrystalline cellulose, *J. Photochem. Photobiol., A*, 2002, **153**, 11–18; (*c*) L. F. Vieira Ferreira, M. R. Vieira Ferreira, A. S. Oliveira, T. J. F. Branco, J. V. Prata and J. C. Moreira, Diffuse reflectance studies of β-phenylpropiophenone and benzophenone inclusion complexes with calix[4], [6] and [8]arenes, *Phys. Chem. Chem. Phys.*, 2002, **4**, 204–210.

4 (*a*) L. F. Vieira Ferreira, J. C. Netto-Ferreira, I. Khmelinskii, A. R. Garcia and S. M. B. Costa, Photochemistry on surfaces: matrix isolation mechanisms for study of interactions of benzophenone adsorbed on microcrystalline cellulose investigated by diffuse reflectance and luminescence techniques, *Langmuir*, 1995, **11**, 231–236; (*b*) L. F. Vieira Ferreira, M. R. Freixo, A. R. Garcia and F. Wilkinson, Photochemistry on surfaces: fluorescence quantum yield determination of dyes adsorbed on microcrystalline cellulose, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 15–22; (*c*) L. F. Vieira Ferreira, A. R. Garcia, M. F. Freixo and S. M. B. Costa, Photochemistry on surfaces: the solvent-matrix effect on the swelling of cellulose. An emission and absorption study of adsorbed auramine-O, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 1937–1944.

5 (*a*) J. P. Da Silva, L. F. Vieira Ferreira, A. M. Da Silva and A. S. Oliveira, A comparative study of the photophysics and photochemistry of 4-chlorophenol adsorbed on silicalite and β-cyclodextrin, *J. Photochem. Photobiol., A*, 2002, **151**, 157–164; (*b*) L. F. Vieira Ferreira, A. S. Oliveira and J. C. Netto-Ferreira, in *Fluorescence Microscopy and Fluorescent Probes 3*, ed. A. Kotyc, Espero Publishing, Prague, 1999, pp. 199–208.

6 L. F. Vieira Ferreira, M. J. Lemos, M. J. Reis and A. M. Botelho do Rego, UV/Vis absorption and luminescence and X-ray photoelectron spectroscopic studies of rhodamine dyes adsorbed onto different pore size silicas, *Langmuir*, 2000, **16**, 5673–5680.

7 D. J. Morantz and A. J. C. Wright, Structures of the excited states of benzil and related dicarbonyl molecules, *J. Chem. Phys.*, 1971, **54**, 692–697.

8 (*a*) R. Dutta and M. Chowdhury, Study of the magnetic field dependent behaviour of radicals generated photochemically from benzil in micellar media, *J. Photochem. Photobiol., A*, 1990, **55**, 197–207; (*b*) K. Bhattacharya and M. Chowdhury, Solvent shift and excited state geometries of benzil, *J. Photochem.*, 1986, **33**, 61–65; (*c*) G. K. Das Mohapatra, J. Bhattacharya, J. Bandopadhyay and S. C. Bera, Flash phololysis of benzils, *J. Photochem. Photobiol., A*, 1987, **40**, 47–58; (*d*) S. C. Bera, R. Mukherjee and M. Chowdhury, Spectra of benzil, *J. Chem. Phys.*, 1969, **51**, 754–761.

9 T. Okutsu, M. Ooyama, K. Tani, H. Hiratsuka, A. Kawai and K. Obi, Kinetic study on the spin polarization switching of benzil in the presence of triethylamine, *J. Phys. Chem. A*, 2001, **105**, 3741–3744.

10 R. W. Fessenden, P. M. Carton, H. Shimamori and J. C. Scaiano, Measurement of the dipole moments of excited states and photochemical transients by microwave dielectric absorption, *J. Phys. Chem.*, 1982, **86**, 3803–3811.

11 (*a*) M. V. Encinas and J. C. Scaiano, Laser photolysis study of the exciplex between triplet benzil and triethylamine, *J. Am. Chem. Soc.*, 1979, **101**, 7740–7741; (*b*) W. G. McGimpsey and J. C. Scaiano, A two photon study of the "reluctant" Norrish type I reaction of benzil, *J. Am. Chem. Soc.*, 1987, **109**, 2179–2181; (*c*) J. C. Scaiano, Photochemical and free-radical processes in benzil-amine systems. Electron-donor properties of α-aminoalkyl radicals, *J. Phys. Chem.*, 1981, **85**, 2851–2855.

12 (*a*) I. Lucak and P. Hrdlvic, Preparation and photochemical properties of 4-propeniyl-benzil polymers, *Macromol. Chem. Phys.*, 1994, **195**, 2233–2245; (*b*) I. Lucak and C. Kosa, The formation of dibenzoyl peroxide by photooxidation of benzil in a polymer film, *Macromol. Rapid Commun.*, 1994, **15**, 929–934.

13 M. Mukai, S. Yamaushi and N. J. Hirota, Time-resolved EPR study on the photochemical reactions of benzil, *J. Phys. Chem.*, 1992, **96**, 3305–3311.

14 (*a*) J. Szejtli, Introduction, general overview of cyclodextrin chemistry, *Chem. Rev.*, 1998, **98**, 1743–1753; (*b*) V. Ramamurthy, Organic photochemistry in organized media, *Tetrahedron*, 1986, **42**, 5753–5839.

15 W. J. Leigh and L. J. Johnson, in *Handbook of Organic Photochemistry*, ed. J. C. Scaiano, CRC Press, Boca Raton, 1989, vol. 1, ch. 2, pp. 401–422.

16 F. Wilkinson and C. J. Wilisher, Triplet-triplet absorption in microcrystalline benzil detected by diffuse reflectance laser flash photolysis, *Appl. Spectrosc.*, 1984, **39**, 897–901.

17 (*a*) C. Huggenberger, J. Lipscher and H. Fisher, Self-termination of benzoyl radicals to ground- and excited-state benzil. Symmetry control of a radical combination, *J. Phys. Chem.*, 1980, **84**, 3467–3474; (*b*) H. Fischer, R. Baer, R. Hany, I. Verhoolen and M. Walbiner, 2,2-Dimetoxy-2-phenylacetophenone: photochemistry and free radical photofragmentation, *J. Chem. Soc., Perkin Trans. 2*, 1990, 787–798.

18 W. Knolle, U. Muller and R. Mehnert, Radiation-induced reactions of benzoyl chloride and acrylates in solution. A pulse radiolysis study, *Phys. Chem. Chem. Phys.*, 2000, **2**, 1425–1430.

19 B. M. Monroe, in *Advances in Photochemistry*, ed. J. N. Pitts, G. S. Hammond and W. A. Noyes. J. Wiley and Sons, New York, 1971, vol. 8, pp. 77–108.

20 T. Hancock-Chen and J. C. Scaiano, Non-linear effects and a cascade of radical events leading to laser-specific generation of active oxygen species, *Photochem. Photobiol.*, 1998, **67**, 174–178.

21 S. Monti, N. Camaioni and P. Bortolus, Photochemistry in a cyclodextrin cavity. Primary processes in the photoreduction of 3- and 4-benzopyridine studied by laser flash-photolysis, *Photochem. Photobiol.*, 1991, **54**, 577–584.

22 M. N. Lehmann, M. G. Bakker, H. Patel, M. L. Partin and S. J. Dormady, The effect of inclusion in β-cyclodextrin on the chemistry of peroxides: Reactions of radicals with β-cyclodextrin, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1995, **23**, 99–117.

23 N. K. Shrestha, E. J. Yagi, Y. Takatori, A. Kawai, Y. Kajii, K. Shibuya and K. Obi, Photochemical α-cleavage reaction of benzoin and its derivatives, *J. Photochem. Photobiol., A*, 1998, **116**, 179–185.

24 F. D. Lewis, R. T. Lanterbach and H. G. Heine, Photochemical α-cleavage of benzoin derivatives. Polar transition states for free radical formation, *J. Am. Chem. Soc.*, 1975, **97**, 1519–1525.